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# STRUCTURAL INTERPRETATION OF THE CONCENTRATION DEPENDENCE OF MOLAR VOLUME IN TERNARY ALUMINOSILICATE GLASSES CONTAINING OXIDES OF THE FIRST AND SECOND GROUPS OF THE PERIODIC SYSTEM

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The concentration dependence of the molar volume of ternary aluminosilicate glasses, in which the content of  $R_2O$  (or  $RO$ ) exceeds the  $Al_2O_3$  content, is determined by the degree of depolymerization of the glass structural lattice. The molar volume in glasses with an equimolar content of  $R_2O$  (or  $RO$ ) and  $Al_2O_3$  is additive and depends on the partial values of the molar volume of the "silica" and "aluminate" components in the structural lattice.

Earlier, we proposed [1, 2] a method for a structural interpretation of the concentration dependence of properties of binary and ternary silicate glasses (using their molar volume as example), which is based on establishing a correlation between the values of a certain considered property and the degree of depolymerization of the silicon-oxygen skeleton (structural lattice) of glass  $R^*$  reflecting the number of non-bridge oxygen ions per one silicon-oxygen tetrahedron. The partial values of the molar volume were determined for a series of modifying oxides of the 1st and 2nd groups of the periodical system, which are proportional to the cube of the radius of the modifying oxide cation and remain constant values over the whole glass-forming region. The error in the estimation of glass molar volume when using the specified partial coefficients, as a rule, amounted to about 1%.

According to the data in [1, 2], the molar volume of glass is calculated using the equation approximating the dependence of the molar volume  $V_m$  on the degree of depolymerization of the glass structural lattice  $R^*$ :

$$V_m = V_{Si} + k_1 R^* + k_2 R^{*2}, \quad (1)$$

where  $V_{Si} = 27.29 \text{ cm}^3/\text{mole}$  is the molar volume of vitreous silica calculated on the basis of its density equal to  $2.202 \text{ g/cm}^3$ ;  $R^* = \Sigma x_j / 2(1 - \Sigma x_j)$ ;  $k_1 = \Sigma k_{1j} x_j / \Sigma x_j$ ;  $k_2 = \Sigma k_{2j} x_j / \Sigma x_j$ ;  $k_{1j}$  and  $k_{2j}$  are the partial coefficients of the modifying oxides;  $x_j$  are the molar parts of the modifying oxides.

The present study analyzed the applicability of the method [1, 2] for approximating the properties of ternary si-

licate glasses containing modifying oxides of the first and the second groups of the periodic system.

According to current concepts [3, 4],  $Al^{3+}$  ions in aluminosilicate glasses can have either four or six oxygen coordination. In the first case, the aluminum-oxygen polyhedra present in glass are tetrahedra  $[AlO_4]$ , and in the second case they are  $[AlO_6]$ . The coordination number of  $Al^{3+}$  ions in aluminosilicate glasses depends on the glass composition, i.e., on the parameter  $\Psi_{Al} = \Sigma x_j / x_{Al}$  which reflects the ratio between the total content of modifier oxides  $R_2O$  and (or)  $RO$  and the content of  $Al_2O_3$ .

With  $\Psi_{Al} \geq 1$ , each oxygen ion brought into the glass by one mole of modifier oxide ensures the modification of the coordination number of two  $Al^{3+}$  ions introduced in one mole of  $Al_2O_3$  from four to six. In this case, all  $Al^{3+}$  ions have four coordination with respect to oxygen and, accordingly, aluminum oxide ( $Al_2O_3$  (IV)) acts as a glass-forming agent, since the aluminum-oxygen tetrahedra are incorporated into the glass structural lattice and form a mixed glass-forming skeleton in which both "siliceous" (consisting of  $[SiO_4]$  tetrahedra) and "aluminate" (consisting of  $[AlO_4]$  tetrahedrons) fragments are present.

With  $\Psi_{Al} < 1$ , the quantity of oxygen ions introduced into the glass with the modifier oxides is insufficient for the modification of the coordination number of  $Al^{3+}$  ions, which preserve their six coordination. In this case, aluminum oxide ( $Al_2O_3$  (VI)) acts as a modifier, since the aluminum-oxygen octahedra are not incorporated into the structural lattice.

The type of relationship of molar volume and the degree of depolymerization of the structural lattice  $R^*$  was analyzed for ternary glasses in which  $\Psi_{Al} \geq 1$ . For this purpose, expe-

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perimental data of various authors on the density of the specified glasses were used.

The molar volume of the glasses was calculated using the formula [3]:

$$V_m = M_m / \rho = \sum m_{mi} x_i / \rho,$$

where  $M_m$  is the molar weight of glass, g/mole;  $\rho$  is the density of glass, g/cm<sup>3</sup>;  $m_{mi}$  are the molar weights of the oxides, g/mole;  $x_i$  is the molar part of the oxides.

It was found that the dependence of the molar volume of the considered glasses on the degree of depolymerization of their structural lattice can be approximated by an equation similar to equation (1):

$$V_m = (V_{Si} + k_{1j} R^* + k_{2j} R^{*2})(1 - 2x_{Al}) + V_{Al(j)} 2x_{Al}, \quad (2)$$

where  $k_{1j}$  and  $k_{2j}$  are coefficients whose physical meaning and numerical values (Table 1) are the same as in equation (1);  $V_{Al(j)}$  are the partial molar volumes of  $Al_2O_3$  (IV), cm<sup>3</sup>/mole, for the given modifying oxide (Table 1) proportional to the cube of the radius of the modifying oxide cation (Fig. 1);  $x_{Al}$  is the molar part of  $Al_2O_3$ .

The physical meaning of the factor  $2x_{Al}$  in equation (2) is expressed by the content of the "aluminate" component in the glass. This value is equal to the sum  $x_{coord} + x_{Al}$  ( $x_{coord}$  is the content of the modifier cations participating in the conversion of  $Al^{3+}$  ions from six coordination to four coordination). Consequently, the factor  $(1 - 2x_{Al})$  in equation (2) reflects the content of the "siliceous" component in the glass.

The physical meaning of the parameter  $R^*$  in equation (2) is the same as in equation (1): i.e., the number of non-bridge oxygen ions per one silicon-oxygen tetrahedron; however, it is calculated using an expression which has a slightly different form:

$$R^* = (x_j - x_{Al}) / 2(1 - x_j - x_{Al}). \quad (3)$$

This difference amounts to the fact that the numerator in equation (3) instead of  $x_j$  uses the difference  $x_j - x_{Al}$  reflecting the number of excess ("active") modifying ions not consumed in the conversion of  $Al^{3+}$  ions to four coordination and taking part in the depolymerization of the glass structural lattice.

TABLE 1

Modifying oxide	$k_{1j}^*$	$k_{2j}^*$	$V_{Al(j)}$
Li <sub>2</sub> O	-33.9	39.4	23.9
Na <sub>2</sub> O	-17.7	22.6	29.1
K <sub>2</sub> O	4.5	7.5	35.1
MgO	-29.0	18.6	21.5
CaO	-24.5	20.3	23.9
SrO	-22.3	22.0	30.1
BaO	-16.9	23.9	35.4

\* Values of  $k_{1j}$  and  $k_{2j}$  are taken from the data in [1].

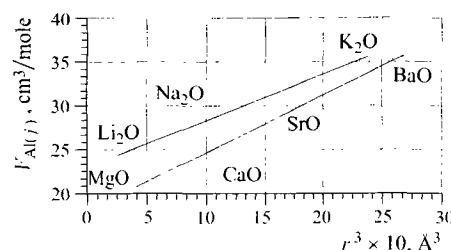


Fig. 1. Dependence of partial molar volume  $V_{Al(j)}$  on the cube of the radius of modifying oxide cations (cation radius values are taken from the data in [5]).

With  $\Psi_{Al} = 1$  (i.e., with  $x_j = x_{Al}$ ), all oxygen ions in the structural lattice become bridge ions [4] and, according to expression (3),  $R^* = 0$ . Accordingly, equation (2) is reduced to the linear form:

$$V_m = V_{Si}(1 - 2x_{Al}) + V_{Al(j)} 2x_{Al}. \quad (4)$$

Thus, in the considered case (with  $\Psi_{Al} = 1$  and  $R^* = 0$ ), the value  $V_m$  essentially characterizes the molar volume of the glass structural lattice  $V_{SS}$ , whose value is additive and is determined by the partial values of the molar volume of the "siliceous" and "aluminate" components. The value  $V_{SS}$  for glasses in which  $\Psi_{Al} > 1$  and  $R^* > 0$ , according to equation (2), can be calculated from the expression

$$V_{SS} = V_m - (k_{1j} R^* + k_{2j} R^{*2})(1 - 2x_{Al}) = V_{Si}(1 - 2x_{Al}) + V_{Al(j)} 2x_{Al}.$$

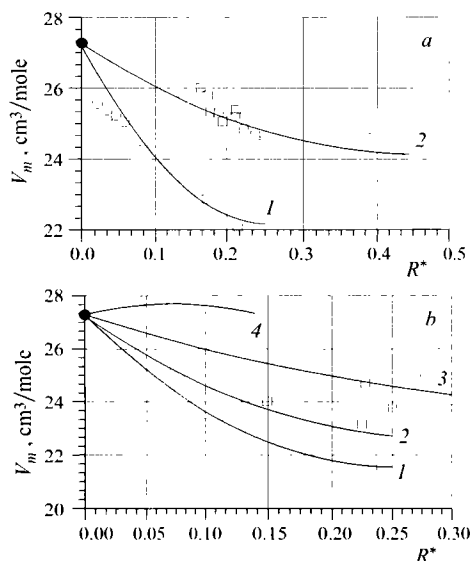
The characteristics of the initial experimental data used in the analysis of the concentration dependence of the molar volume of ternary aluminosilicate glasses containing various oxides of the first and second groups, as well as the mean square error values in calculating  $V_m$ , are given in Table 2.

The obtained results point to the possibility of using the methods described in [1, 2] to approximate the concentration dependence of properties of ternary aluminosilicate glasses containing various modifying oxides of the first and second groups of the periodical system (Table 2, Figs. 2 and 3).

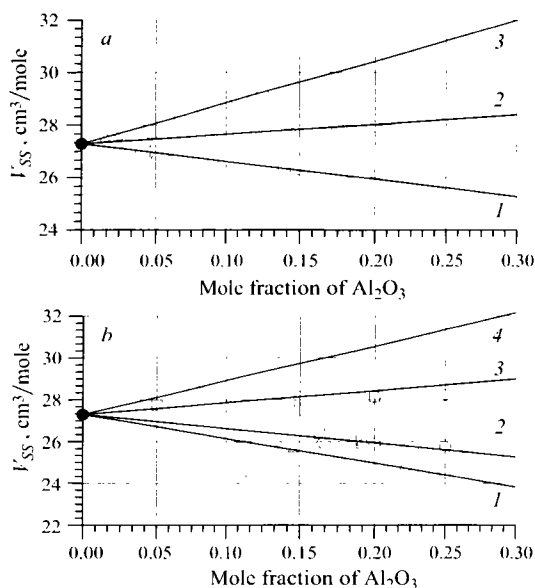
In the case of glasses where  $\Psi_{Al} > 1$  and  $R^* > 0$ , the observed concentration dependence of the molar volume (simi-

TABLE 2

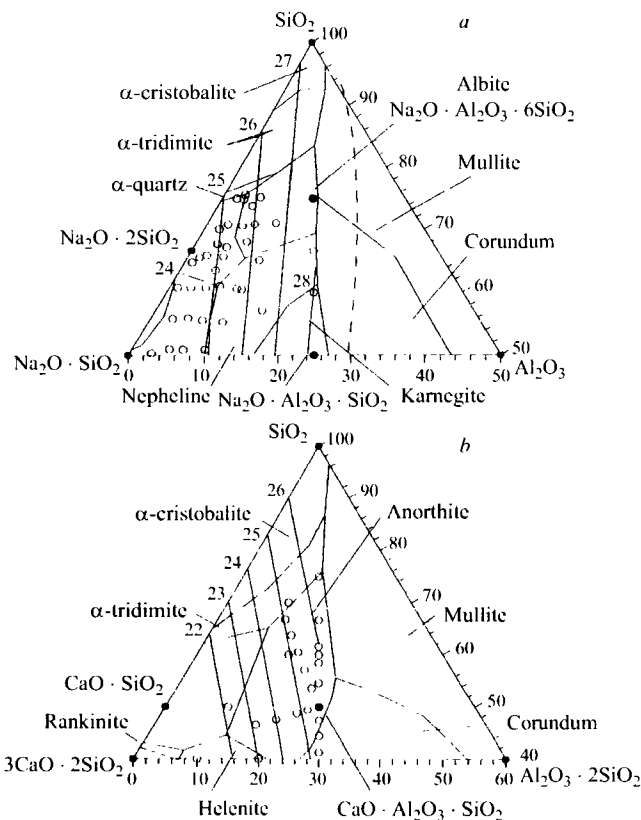
System	Relative mean square error in estimating $V_m$ , %	Number of glass compositions used in data processing	Published source
Li <sub>2</sub> O - Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	0.97	46	[6 - 8]
Na <sub>2</sub> O - Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	0.66	38	[6]
K <sub>2</sub> O - Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	0.27	5	[9]
MgO - Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	1.47	8	[6]
CaO - Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	1.61	27	[6]
SrO - Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	2.67	17	[6]
BaO - Al <sub>2</sub> O <sub>3</sub> - SiO <sub>2</sub>	0.18	2	[6]



**Fig. 2.** Concentration dependences of molar volume  $V_m$  of glasses in systems  $R_2O-Al_2O_3-SiO_2$  (a) and  $RO-Al_2O_3-SiO_2$  (b):  $R_2O$ ,  $RO$  -  $Li_2O$ ,  $MgO$  (1);  $Na_2O$ ,  $CaO$  (2);  $SrO$  (3);  $BaO$  (4); continuous lines) estimated values; dots) experimental data of various authors (Table 2) for glasses with a constant content of the modifying oxide and a variable content of  $Al_2O_3$ ;  $x$ )  $cR_2O \cdot xAl_2O_3 \cdot (1 - c - x)SiO_2$ ;  $\circ$ )  $c = 0.15$  for  $Li_2O$  and  $BaO$ ,  $c = 0.40$  for  $SrO$ ;  $\diamond$ )  $c = 0.20$  for  $Li_2O$  and  $Na_2O$ ;  $\Delta$ )  $c = 0.25$  for  $Li_2O$ , 0.28 for  $MgO$ , 0.23 for  $CaO$ , 0.22 for  $BaO$ ;  $\square$ )  $c = 0.30$  for  $Li_2O$  and  $Na_2O$ , 0.35 for  $MgO$ ,  $CaO$ , and  $SrO$ ;  $\nabla$ )  $c = 0.45$  for  $Na_2O$ ;  $\bullet$ ) value of  $V_m$  for vitreous  $SiO_2$ .



**Fig. 3.** Concentration dependences of the parameter  $V_{SS}$  of glasses in systems  $R_2O-Al_2O_3-SiO_2$  (a) and  $RO-Al_2O_3-SiO_2$  (b):  $R_2O$ ,  $RO$  -  $Li_2O$ ,  $MgO$  (1);  $Na_2O$ ,  $CaO$  (2);  $K_2O$ ,  $SrO$  (3);  $BaO$  (4); continuous lines) estimated values; dots) experimental data of various authors (Table 2) for glasses with a constant content of the modifying oxide and a variable content  $x$  of  $Al_2O_3$  of the same compositions as in Fig. 2 and glasses with an equimolecular content of the modifying oxide and  $Al_2O_3$  including  $K_2O$ ,  $MgO$ , and  $CaO$  ( $\circ$ ).



**Fig. 4.** Correlation of the concentration dependence of the molar volume of glasses in the systems  $Na_2O-Al_2O_3-SiO_2$  (a) and  $CaO-Al_2O_3-SiO_2$  (b) and the structural specifics of the respective phase diagrams: Dashed line) boundary of the glass-forming region in  $Na_2O-Al_2O_3-SiO_2$  system (data from the reference book [6]);  $\bullet$ ) compositions of the compounds formed in the systems; boundaries of primary crystallization fields) data from the reference book [12];  $\circ$ ) experimental values of glass compositions (Table 2); continuous lines) estimated values of molar volume; numerical indexes on the continuous lines are isovalues of  $V_m$  (cm³/mole).

lar to the case of silicate glasses not containing  $Al_2O_3$  [1, 2]) is determined by the degree of depolymerization of the structural lattice and is determined by the effects of its compaction and loosening discussed in [1].

In the case of glasses in which  $\Psi_{Al} = 1$  and  $R^* = 0$ , the concentration dependence of the molar volume becomes linear (equation (4)) and essentially illustrates the additivity of the molar volume  $V_{SS}$  of the glass structural lattice. The linear concentration dependence of the parameter  $V_{SS}$ , i.e., the additivity of  $V_{SS}$ , is also preserved in glasses in which  $\Psi_{Al} > 1$  and  $R^* > 0$  (Fig. 3).

Since the partial molar volume value of  $Al_2O_3$  (IV) is not constant and varies depending on the type of modifying oxides present in glasses (Table 2), it can be assumed that the modifying cations participating in the modification of the coordination of  $Al^{3+}$  ions occupy certain preferential positions through association with the "aluminate" fragments of the structural lattice.

Based on equation (2), it is possible to develop a computer program making it possible to determine the compositions of ternary aluminosilicate glasses with a prescribed constant value of molar volume, and based on the obtained data, plot isolines  $V_m$  on the concentration triangle or on a ternary phase diagram. The latter makes it possible to correlate the concentration dependence of  $V_m$  in glasses with the structural specifics of the respective phase diagrams.

Such calculations and plotting in the present study were performed for glasses of the  $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  and  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  systems. It was found (Fig. 4) that the concentration dependence of the molar value of ternary aluminosilicate glasses in the specified systems, as in the case of binary and ternary silicate glasses not containing  $\text{Al}_2\text{O}_3$  [1, 2], have a smooth monotonic shape and do not exhibit any breaks when transgressing the phase boundaries (primary crystallization fields) in the considered phase diagrams. This agrees with the conclusions in [10] and points to the fact that the representation of the concentration dependence of silicate glass properties performed in several papers [11] using rational functions correlating with the phase diagram fields are in fact just a certain approximation.

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